PROJECT NUMBER: 2515

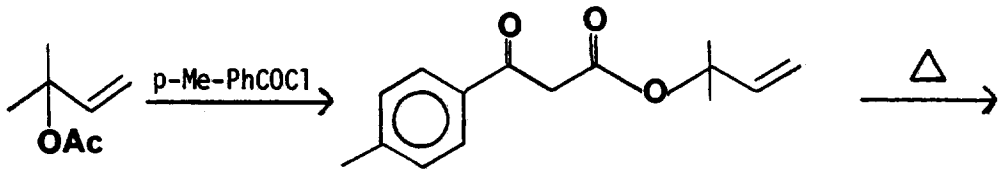
PROJECT TITLE: Flavor-Release Chemistry

PROJECT LEADER: Y. Houminer

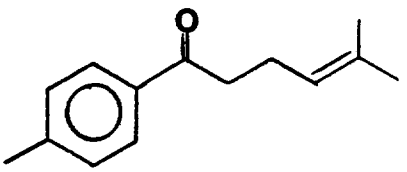
PERIOD COVERED: August 1-31, 1981

DATE OF REPORT: September 8, 1981

Last month we reported the discovery of an unusual rearrangement-decarboxylation of allylic β-ketoesters to generate homoallylic ketones. To test the generality of this reaction, 2-methyl-3-buten-2-yl acetate was prepared and its anion was reacted with p-methylbenzoyl chloride to give the desired keto-ester(I).[1] Pyrolysis of the latter at 200°C for 15 min. gave 71% of the rearranged ketone (II), thus demonstrating the generality of this reaction.[1] To the best of our knowledge this reaction which resembles the ester enolate Claisen rearrangement has not yet been reported in the literature. It has a great synthetic potential and we plan to study it with different allylic functional groups.



I



II

We have started to explore the release of alcohols and phenols from systems derived from esters of 4-hydroxyvaleric acid. Ethyl 2-isopropyl-5-oxo-hexanoate (III) was reduced with $NaBH_4$ to yield the corresponding hydroxy-ester (IV).[2] Pyrolysis of the latter at 200°C for 10 min. did not release ethanol and the starting material was left unchanged.[2] It is expected however, that more reactive esters such as phenyl esters will undergo this reaction at relatively low temperatures.

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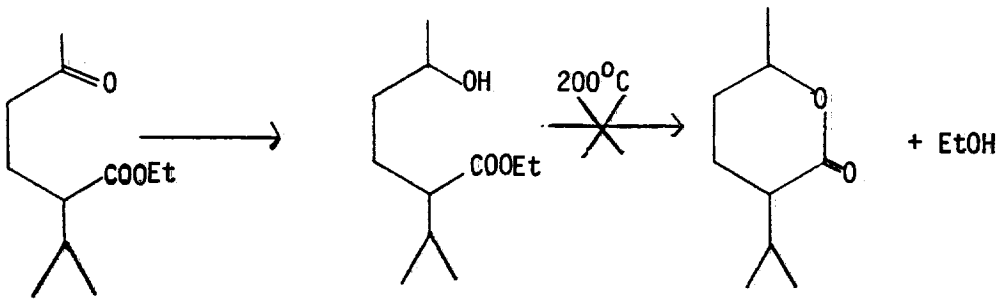
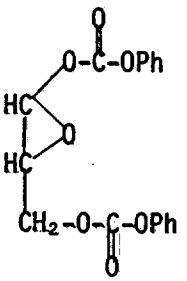


III IV

Our research in the area of glycerol-based release systems has been extended to include also glyceraldehyde. In an attempt to peracylate the hydroxy groups with phenyl chloroformate an unexpected product was obtained (V).[3] This very interesting bis-carbonate will be tested as a potential release system for phenols.



V

Encouraged by the good yield of phenol released in the pyrolysis of 1-O-phenylcellobioside we extended this study to 1-O-(2-methoxy-4-methylphenyl)cellobioside. 1-O-(2-methoxy-4-methylphenyl)-2,3,6,2',3',4',6' heptacetyl cellobiose was prepared in 65% yield from the octoacetate.[1] Removal of the acetyl protecting groups is now in progress.

The reaction of 2-ethylpyrazine anion with benzaldehyde was repeated to yield 15% of the expected product 2-(2-hydroxy-1-methyl-2-phenylethyl) pyrazine as a 1:1 mixture of diastereoisomers. The two isomers were separated by preparative t.l.c.[3] Additional purification of these isomers is required before their pyrolysis can be studied.

References

1. G. Chan 7462
2. Y. Houminer 7424
3. K. Podraza 7591

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